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Spectral and Biological Studies on Organotin(IV) Complexes of Heterocyclic Benzothiazolines

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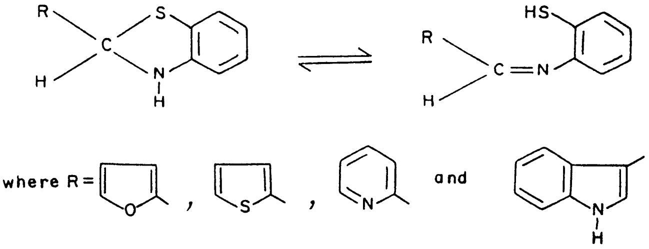
Synopsis. The monobasic bidentate benzothiazolines, which were produced by the reaction of 2-mercaptoaniline and the heterocyclic aldehydes e.g., 2-furaldehyde, 2-thiophenecarbaldehyde, 2-pyridinecarbaldehyde, and 3-indolecarbaldehyde, have reacted with dialkyltin dichloride to give colored compounds. These compounds were characterized on the basis of elemental analyses, molar conductance, molecular weight determination, electronic and infrared spectral studies. Multinuclear NMR(^{1}H, ^{13}C, and ^{119}Sn) data suggest trigonal bipyramidal and octahedral geometries for the resulting $Me_2SnCl(\widehat{NS})$ and $Me_2Sn(\widehat{NS})_2$ type complexes where $\widehat{NS}$ indicates benzothiazoline ligand, respectively. The fungitoxicity of 2-(2-thienyl)benzothiazoline and its complexes has been evaluated on pathogenic fungi.

During the recent years, much interest has been shown in the synthesis of metal chelates with sulfur containing ligands due to their different biological applications.[1,2] It has, however, been reported that on complexation[3,4] the activity of sulfur-containing ligands increases still further. Our continuing interest in the synthesis of biologically active complexes have led us to prepare and study the structures as well as other features of organotin complexes of heterocyclic benzothiazolines. The equilibrium forms of the ligands used during these investigations are shown below:



Experimental

Chemicals and solvents used were dried and purified by standard methods and moisture was excluded from the glass apparatus using $CaCl_2$ guard tubes. The ligands were prepared as reported in our earlier publication.[5]

Preparation of Complexes. To a weighed amount of dimethyltin dichloride in ca. 30 cm^3 of dry methanol in 100 cm^3 R.B. flask, was added the calculated amount of sodium salt of the ligand in 1 : 1 and 1 : 2 molar ratios. The mixture was heated under reflux for about 6 hours and the precipitate of sodium chloride so formed was filtered off. The solvent was removed and the product dried in vacuo. It was repeatedly washed with dry cyclohexane and again dried in vacuo. The physical properties and analytical data of these complexes are recorded in Table 1.

^{1}H NMR spectra were recorded on a JEOL FX 90Q spectrometer in DMSO-d_6 at 89.55 MHz, and ^{13}C and ^{119}Sn NMR spectra in methanol at 22.49 MHz and 33.35 MHz, respectively. Other methods of analyses and physical measurements are same as reported earlier.[5,6]

Results and Discussion

The reactions of dimethyltin dichloride with benzothiazolines (abbrev. to $\widehat{NS}$) in 1 : 1 and 1 : 2 molar ratios proceed as follows:

$$Me_2SnCl_2 + \widehat{NS}Na \xrightarrow[1:1]{MeOH} Me_2SnCl(\widehat{NS}) + NaCl$$

$$Me_2SnCl_2 + \widehat{NS}Na \xrightarrow[1:2]{MeOH} Me_2SnCl(\widehat{NS})_2 + NaCl$$

All the newly synthesized complexes are colored solids and soluble in most of the common organic solvents. The low values of molar conductance (15—20 ohm^{-1} cm^2 mol^{-1}) in anhydrous *N*,*N*-dimethylformamide show them to be nonelectrolytic in nature. The molecular weight determinations show them to be monomeric.

The electronic spectra of the ligands consist of two bands around 250 nm and 315 nm characteristic of benzothiazolines.[8] These bands arise out of θ-θ^* and π-π^* benzenoid[8] transitions and which remain almost unchanged in all the tin complexes. However, an additional band is also observed in the region 390—410 nm due to n-π^* electronic transitions of the azomethine[8] and which indicates rearrangement of the ligands to the imine on complexation.

In the IR spectra of the ligands strong bands in the regions 3370—3200 cm^{-1} and 1670—1705 cm^{-1} due to NH stretching and deformation vibrations, respectively are observed. The absence of ν(SH) at 2500—2600 cm^{-1} and ν(C=N) at 1600—1650 cm^{-1} is indicative of the benzothiazolines.[9] In complexes, the bands due to NH vibrations are not observed and this indicates the chelation of nitrogen with the tin atom. A new band at ca. 1600 cm^{-1} in the spectra of complexes due to ν(C=N) vibrations suggests that the complexes are metal-Schiff base derivatives as the benzothiazoline ring rearranges to give the Schiff base derivatives in the presence of metal ion.[8] Several new bands in the spectra of tin complexes[6] in the regions 390—450, 325±20, and 280±15 cm^{-1} may be assigned to ν Sn←N, ν Sn-S, and ν Sn-Cl respectively, and this lends further support to the proposed coordication in these complexes.

^{1}H NMR spectral studies further support the bonding pattern as discussed above. The N-H proton signals at δ 4.20 (2-furyl-BztH) and δ 4.36 (2-thienyl-BztH) in the spectra of benzothiazolines disappear in the corresponding tin complexes. The azomethine proton signal shifts down field in the spectra of complexes due to the formation of a coordinate linkage

Table 1. Analyses and Physical Characterics of Organotin Complexes

Compound[a]	Color and state	Mp θ_m/°C	Yield %	Analysis/% C Found (Calcd)	H Found (Calcd)	N Found (Calcd)	S Found (Calcd)	Cl Found (Calcd)	Sn Found (Calcd)
Me_2SnCl(2-furyl-Bzt)	Yellow solid	190	73	40.15	3.32	3.24	8.03	8.95	30.30
				(40.39)	(3.63)	(3.63)	(8.29)	(9.19)	(30.73)
Me_2Sn(2-furyl-Bzt)$_2$	Yellow solid	198	72	45.01	3.46	4.52	10.53	—	19.89
				(49.26)	(3.76)	(4.79)	(10.95)		(20.29)
Me_2SnCl(2-thienyl-Bzt)	Green solid	240d[b]	78	38.55	3.23	3.15	15.63	8.52	29.27
				(38.79)	(3.48)	(3.48)	(15.91)	(8.83)	(29.51)
Me_2Sn(2-thienyl-Bzt)$_2$	Yellowish brown solid	235	75	49.00	3.45	4.38	21.56	—	20.00
				(49.26)	(3.76)	(4.79)	(21.89)		(20.31)
Me_2SnCl(3-indolyl-Bzt)	Brown solid	115d	71	46.65	3.66	6.23	7.10	7.88	26.95
				(46.88)	(3.91)	(6.43)	(7.35)	(8.15)	(27.27)
Me_2Sn(3-indolyl-Bzt)$_2$	Dark brown solid	133	69	58.81	4.01	8.30	9.71	—	18.00
				(59.01)	(4.30)	(8.61)	(9.84)		(18.24)
Me_2SnCl(2-pyridyl-Bzt)	Grey solid	232	78	41.85	3.53	6.81	7.95	8.54	29.57
				(42.29)	(3.78)	(7.05)	(8.06)	(8.94)	(29.88)
Me_2Sn(2-pyridyl-Bzt)$_2$	Dark yellow solid	215d	77	53.92	4.00	9.42	10.94	—	20.31
				(54.29)	(4.18)	(9.74)	(11.14)		(20.65)

a) Benzothiazoline is abbreviated to Bzt which are 2-(2-furyl)benzothiazoline, 2-(2-thienyl)benzothiazoline, 2-(3-indolyl)benzothiazoline, and 2-(2-pyridyl)benzothiazoline. b) d=decomp.

Table 2. ^{13}C NMR Spectral Data for Benzothiazoline and Its Corresponding Tin Complexes

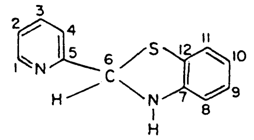
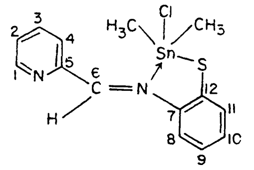
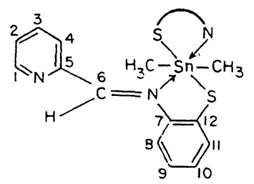
	1	2	3	4	5	6	7	8	9	10	11	12	Sn-C
	123.46	121.89	120.64	121.19	125.52	149.57	126.17	125.95	125.61	125.42	126.77	136.92	—
	123.64	121.92	120.72	121.23	125.83	151.32	126.71	126.12	126.43	126.59	127.13	139.24	17.92
	123.72	121.90	120.87	121.22	125.85	153.32	126.75	126.31	126.32	126.42	127.82	140.23	16.85

Table 3. Fungicidal Screening Data of Ligand and Its Complexes

Compound	Average percentage inhibition after 96 h Organism Helminthosporium gramineum concn used 0.01%	0.1%	Organism Rhizopus oryzae concn used 0.01%	0.1%	Organism Aspergillus concn used 0.01%	0.1%
2-Thienyl-BztH	37	41	34	46	41	53
Me_2SnCl(2-thienyl-Bzt)	58	68	65	85	70	84
Me_2Sn(2-thienyl-Bzt)$_2$	56	71	60	79	63	85

between nitrogen and tin atoms. The protons of the methyl groups appear at δ 1.12, 1.34, 1.08, and 1.33 in the tin complexes.

^{13}C NMR spectra of 2-(2-pyridyl)benzothiazoline and its 1 : 1 and 1 : 2 tin complexes were also recorded (Table 2). The considerable shifts in the positions of carbons of the tin complexes marked by (6) and (12) attached to N and S, respectively, clearly indicate that the nitrogen and sulfur of the mercapto group participate in complexation reaction as discussed earlier.

The compound Me_2SnCl(2-pyridyl-Bzt) gives a signal at −147 ppm in the ^{119}Sn NMR indicative of five-coordination around the tin atom as it is in agreement with the previously reported values.[10]

On the basis of the foregoing discussions, trigonal bipyramidal and octahedral geometries around the tin atom have been proposed in 1 : 1 and 1 : 2 tin complexes, respectively.

Evaluation of the Antifungal Activity. Helminthosporium gramineum, Rhizopus oryzae and Aspergillus flavus were employed to check the antifungal activity of the benzothiazoline and its 1 : 1 and 1 : 2 complexes. The results of the antifungal activity given in Table 3 show that Me_2Sn(2-thienyl-Bzt$)_2$ shows almost complete inhibition in higher concentration. As compared to 2-(2-thienyl)benzothiazoline, Me_2SnCl(2-thienyl-Bzt) and Me_2Sn(2-thienyl-Bzt$)_2$ exhibit greater fungitoxicity against all the fungi. The fungitoxicity of ligand and its complexes decreases on lowering the concentration. The increased fungitoxicity of the complexes as compared to the ligand may be due to chelation as the polarity of the metal ion in the complexes which reduces considerably due to the partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring system. This in turn increases the hydrophobic character of the metal favoring its permeation through the lipoid layers of the fungal membranes.[11]

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References

1) N. P. Buu-Hoi, T. B. Voc, and N. D. Xuong, *Bull. Soc. Chim. Fr.*, **1955**, 694.

2) B. G. Benns, B. A. Gingras, and C. H. Bayley, *App. Microbiol.*, **8**, 353 (1960).

3) Y. Skada, Jpn. Patent 7017189 (1970); *Chem. Abstr.*, **73**, 77252y (1970).

4) R. S. Srivastava, *J. Inorg. Nucl. Chem.*, **42**, 1526 (1980).

5) Mrs. K. Singh, R. V. Singh, and J. P. Tandon, *Inorg. Chim. Acta*, **151**, 179 (1988).

6) Mrs. K. Singh, R. V. Singh, and J. P. Tandon, *Synth. React. Inorg. Met-Org. Chem.*, **16**, 1341 (1986) and references therein.

7) J. G. Horsfall, *Bot. Rev.*, **11**, 357 (1945).

8) R. V. Singh and J. P. Tandon, *Synth. React. Inorg. Met-Org. Chem.*, **11**, 109 (1981).

9) H. Jadamus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, **86**, 3056 (1964).

10) S. J. Blunden and P. J. Smith, *J. Organomet. Chem.*, **157**, 226 (1982).

11) R. S. Srivastava, *Inorg. Chim. Acta*, **56**, 165 (1981).